

# Few-layer MoS<sub>2</sub> saturable absorbers for short-pulse laser technology: current status and future perspectives [Invited]

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compiled: February 11, 2015

Few-layer molybdenum disulfide (MoS<sub>2</sub>) is emerging as a promising quasi-two-dimensional material, further extending the library of suitable layered nanomaterials with exceptional optical properties for use in saturable absorber devices that enable short-pulse generation in laser systems. In this article, we catalog and review the nonlinear optical properties of few-layer MoS<sub>2</sub>, summarize recent progress in processing and integration into saturable absorber devices and comment on the current status and future perspectives of MoS<sub>2</sub>-based pulsed lasers.

*OCIS codes:* (140.3538) Lasers, pulsed; (160.4236) Nanomaterials; (160.4330) Nonlinear optical materials; (230.4320) Nonlinear optical devices.

<http://dx.doi.org/10.1364/XX.99.099999>

## 1. Introduction

Short-pulse lasers are becoming ubiquitous tools in a wide variety of applications, including industrial materials processing, biomedical imaging and fundamental research [1–4]. This is driven by advances in saturable absorber (SA) technologies, in addition to new gain media [5, 6], enabling more versatile pulse sources. A saturable absorber acts as a passive optical switch in a laser cavity to enable short-pulse generation by passive mode-locking or Q-switching [1]. The current dominant saturable absorber technologies, such as semiconductor saturable absorber mirrors (SESAMs) and nonlinear polarization evolution (NPE) possess limitations – for example, SESAMs typically exhibit narrowband operation and limited ( $\sim$ picosecond) response times without post-processing [7, 8] and NPE is highly sensitive to environmental fluctuations [9] – driving research to consider alternative materials with nonlinear optical properties for SAs, and other novel photonic devices.

Intense research into the field of low-dimensional nanomaterials has recently demonstrated that one-dimensional (1D) and quasi-1D nanomaterials, such as single- and multi-wall carbon nanotubes (CNTs) formed of single or few atomic layer thick tubes of atoms respectively [10, 11], and two-dimensional (2D) and quasi-2D nanomaterials, such as mono- and few-layer graphene [12, 13] consisting of mono- or few-layers of atoms, exhibit remarkable optical and electrical properties and environmental robustness [11, 13]. This suggests

their suitability as candidate materials for the development of future photonic technologies [11, 13]. While carbon nanotubes [14, 15] and graphene [16, 17] have emerged as promising materials for saturable absorber devices, as well as a more general platform for novel optoelectronic systems [11, 13], they are only two examples of a wider class of nanomaterials that are currently being investigated, including few-layer transition-metal dichalcogenides [18] and quasi-2D topological insulators [19]. These other nanomaterials offer distinct yet complementary properties to carbon nanotubes and graphene [18, 19].

Transition metal dichalcogenides (TMDs) are semiconductors of the form MX<sub>2</sub>, with a layered crystal structure [20]. Each layer consists of a single plane of hexagonally-arranged transition metal (M) atoms (e.g. Mo, W) held between two hexagonal planes of chalcogen (X) atoms (e.g. S, Se) by strong covalent bonds [Fig. 1(a)] [20]. In bulk form, individual MX<sub>2</sub> layers are held together by relatively weak van der Waals forces [20], which has enabled monolayer (2D) and few-layer (quasi-2D) flakes of TMD materials to be exfoliated. The optical and electronic properties of such flakes has been found to be strongly thickness-dependent, with monolayer and bulk forms possessing distinct properties [18]. Recently, the TMD molybdenum disulfide (MoS<sub>2</sub>) has received particular attention, in part due to its availability from naturally occurring molybdenite [21]. In bulk form, MoS<sub>2</sub> has an indirect 1.29 eV (961 nm) bandgap, whereas monolayer MoS<sub>2</sub> is a non-centrosymmetric material with a direct 1.80 eV (689 nm) energy gap [22]. Contemporary studies have highlighted the favorable optoelectronic properties of mono-

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layer and few-layer MoS<sub>2</sub>, including strong photoluminescence [23], current on/off ratios exceeding 10<sup>8</sup> in field-effect transistors [24], and a nonlinear optical response stronger than that of graphene [25], paving the way for the development of new photonic devices, such as SAs for pulsed laser technology.

Reports of few-layer MoS<sub>2</sub> and observations of their thickness-dependent properties first appeared in the literature many decades before the graphene-led renaissance in 2D materials [26]. In 1963 Frindt and Yoffe considered the optical properties of thin (<10 nm thick) MoS<sub>2</sub> crystals, later identifying new features in the absorption spectrum of few-layer MoS<sub>2</sub> flakes (mechanically exfoliated with adhesive tape) [27–29]. Reports of monolayer exfoliation using lithium-based intercalation techniques were also published [30]. However, early studies were limited by the instrumentation and techniques available for characterization that would not meet today’s standards for imaging single and few atomic layers; neither the nonlinear optical properties of few-layer MoS<sub>2</sub> nor the technological benefits were exploited.

In this review, we consider the current state of few-layer MoS<sub>2</sub>-based photonics, with a particular focus on fabrication techniques, integration strategies, and nonlinear optical properties and applications. We catalog the properties of MoS<sub>2</sub> SA devices, and the performance parameters of MoS<sub>2</sub>-based short-pulse lasers, to date. It is concluded that few-layer MoS<sub>2</sub> could play a significant role in future optoelectronic and photonic technologies, particularly as a wideband saturable absorber for versatile pulsed laser sources.

## 2. Processing and Device Integration

A variety of techniques exist for producing mono- and few-layer MoS<sub>2</sub> flakes, complemented by a range of flexible integration platforms for including flakes in practical devices for target applications [18]. To commercially exploit such devices, modern manufacturing techniques are required for large-scale, low-cost fabrication of few-layer materials [31].

In this section, we briefly consider: the processing of MoS<sub>2</sub> flakes; the characterization techniques available to quantify flake size and number of layers; and the integration platforms used for the development of SA devices. We conclude with a manufacturing case study, outlining the steps involved in the production of few-layer MoS<sub>2</sub>-PVA composite films.

### 2.A. Monolayer and Few-Layer MoS<sub>2</sub> Fabrication

Few-layer fabrication techniques can be broadly separated into two approaches [18, 31, 32]: top-down exfoliation (including mechanical cleavage and solution processing techniques) and bottom-up growth (such as chemical vapor deposition and pulsed laser deposition). It should be noted that there is no standardized agreement for the number of MoS<sub>2</sub> layers required for classification as ‘few-layer MoS<sub>2</sub>’ compared to bulk MoS<sub>2</sub>; in the graphene-community, few-layer graphene is generally accepted to consist of fewer than 10 monolayers

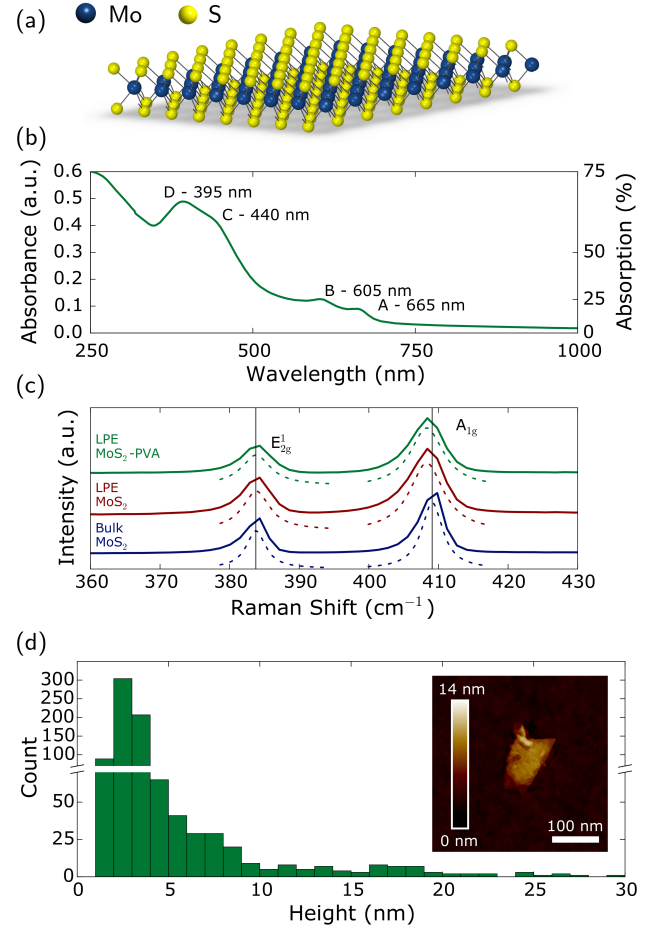


Fig. 1. (a) Illustration of MoS<sub>2</sub> monolayer. (b) Linear optical absorption of MoS<sub>2</sub> dispersion. (c) Raman spectra for the bulk MoS<sub>2</sub>, LPE MoS<sub>2</sub> and a MoS<sub>2</sub>-polymer composite film. The vertical lines show the peak positions for bulk MoS<sub>2</sub> (obtained by Lorentzian fitting, as shown beneath each peak), highlighting the difference in peak position for LPE and bulk MoS<sub>2</sub>. (d) Distribution of flake thicknesses measured via AFM (inset: typical AFM image of MoS<sub>2</sub> flake deposited on Si/SiO<sub>2</sub>).

[26], however, in this review, we include reports in the literature of few-layer MoS<sub>2</sub> with up to 30 layers.

Mechanical exfoliation involves repeatedly cleaving layers from bulk layered crystal materials, often using adhesive tape, leaving few-layer and a small number of monolayer flakes [18, 33]. This was the first reported technique for obtaining few-layer flakes of MoS<sub>2</sub> [28] and can be used to produce high-quality, single-crystal flakes [33]. However, despite widespread usage of the mechanical cleavage technique for fundamental studies of 2D materials [23, 33, 34], poor scalability and low yield render it unsuitable for realistic large-scale applications.

Chemical vapor deposition (CVD) growth offers a scalable method for the production of single- and few-layer MoS<sub>2</sub> [35, 36]. For example, solid precursors MoO<sub>3</sub> and sulfur are heated in a furnace to ~650°C [37]. The

sulfur vapor reduces the  $\text{MoO}_3$ , first forming volatile  $\text{MoO}_{3-x}$  compounds before being catalyzed by the substrate to form a single- or few-layer film of  $\text{MoS}_2$  [37–40]. The film growth is limited by the low nucleation rate on bare substrates and pre-treatment of the substrate is often necessary to seed the  $\text{MoS}_2$  growth [40].

Another growth technique is hydrothermal synthesis, where crystallization is achieved at a high vapor pressure reaction and elevated temperatures. In Ref. [41], few-layer  $\text{MoS}_2$  flakes were fabricated by a hydrothermal reaction between  $\text{NaMoO}_4$  and  $\text{SiO}_2 \cdot 12\text{WO}_2 \cdot x\text{H}_2\text{O}$  at  $240^\circ\text{C}$  for 24 hours with thiourea as the sulfurization reagent. However, the mechanism for the formation of the nanosheets from the reaction is not explained.

Pulsed laser deposition (PLD) produces films of material following ablation from a target, such as bulk  $\text{MoS}_2$  crystals [42, 43]. The target is placed in a chamber (typically under vacuum), and irradiated, producing a plume of ejecta which can deposit onto a substrate. In particular, the technique allows control over the ratio of molybdenum to sulfur in the film due to the different evaporation rates of the two ions [43].

Solution processing is a widely used technique that produces a high yield of mono- and few-layer flakes dispersed in liquid, carried out under ambient conditions with a high throughput [31].  $\text{MoS}_2$  can either be chemically exfoliated (e.g. via lithium intercalation) [30, 44, 45] or dispersed into select solvents via liquid phase exfoliation (LPE) [46].

Chemical exfoliation of  $\text{MoS}_2$  is typically achieved via lithium intercalation followed by hydrothermal exfoliation [30, 44, 45, 47–49]. The intercalant increases the separation between  $\text{MoS}_2$  layers, allowing exfoliation into solvents via stirring or ultrasonication [30, 44, 45]. The use of lithium compounds as an intercalant enhances the process via the release of hydrogen on exposure to water [30]. However, exfoliation of  $\text{MoS}_2$  by this method can lead to structural alterations in the material [44, 50], producing the 1T  $\text{MoS}_2$  phase, and requiring annealing at  $\sim 300^\circ\text{C}$  to restore the 2H phase of untreated  $\text{MoS}_2$  [44]. The 2H and 1T phases of  $\text{MoS}_2$  differ in the coordination of the Mo atoms, which is trigonal prismatic in the 2H phase and octahedral in the 1T phase [44, 50, 51]. Unlike 2H- $\text{MoS}_2$ , 1T- $\text{MoS}_2$  is metallic, due to degeneracies in the band-structure [52]. The presence of 1T- $\text{MoS}_2$  in intercalated samples is evidenced by the absence of photoluminescence, even in monolayer flakes [44], as well as by differences in the Raman and optical absorption spectra [44].

LPE involves three main steps: 1) dispersion of bulk  $\text{MoS}_2$  in a solvent; 2) exfoliation; 3) purification [32]. First, bulk  $\text{MoS}_2$  is dispersed in a suitable solvent (one that minimizes the interfacial tension between the liquid and material [53]). Ultrasound-assisted exfoliation is then used to exfoliate few-layer  $\text{MoS}_2$  flakes from the bulk by cavitation waves (from the formation, growth and collapse of bubbles and voids in the liquid due to pressure fluctuations [54]). Finally, exfoliated few-layer

flakes are separated from unexfoliated thick flakes, usually performed using ultracentrifugation. Ultracentrifugation also enables sorting of  $\text{MoS}_2$  flakes by thickness, providing a route to engineering  $\text{MoS}_2$  dispersions with desired flake sizes [55].

Finally, we note that other few-layer  $\text{MoS}_2$  fabrication techniques exist such as physical vapor deposition [40] and gas phase growth [56], although here we have restricted the scope of our review to those which, to date, have been used to produce SA devices.

## 2.B. Material Characterization

### 2.B.1. Raman Spectroscopy

Raman Spectroscopy is very a popular tool to study crystal quality [34, 57] as well as accurately determine the number of layers in  $\text{MoS}_2$  flakes [57].  $\text{MoS}_2$  has four Raman-active modes ( $E_{1g}$ ,  $E_{2g}^1$ ,  $A_{1g}$  and  $E_{2g}^2$ ) and two IR-active modes ( $A_{2u}$  and  $E_{1u}$ ) [58, 59]. The  $E_{2g}^1$  is an in-plane mode generated by the opposing vibration of the two S atoms with respect to the Mo atom, while the  $A_{1g}$  mode comes from the out-of plane modes of S atoms in opposite directions. From monolayer to bulk, the  $E_{2g}^1$  mode red shifts [57, 59]. This has been attributed to an enhancement of the dielectric screening of the long-range Coulomb interaction between the effective charges with a growing number of layers [59]. On the other hand the  $A_{1g}$  mode blue shifts as it is less sensitive to the inter-layer coupling [60, 61] while it is sensitive to adsorbates. The frequency shift between  $E_{2g}^1$  and  $A_{1g}$  modes is often used to determine the number of layers [57]. Several other Raman-active modes have been identified at low-frequency (around  $7\text{ cm}^{-1}$  and  $25\text{ cm}^{-1}$ ) for multi-layer  $\text{MoS}_2$  flakes [62]. In single layer  $\text{MoS}_2$  there are no rigid-layer vibrations [62]. For multi-layer  $\text{MoS}_2$  these have been grouped into shear modes (C) and layer breathing modes (LBMs). C modes red-shift while LBMs blue-shift with increasing number of layers [62]. It is however important to note that there are multiple factors affecting the different Raman modes active in  $\text{MoS}_2$  (inter-layer coupling, coulomb interaction, breathing modes, adsorbates, doping, etc.) making it impossible to generate a complete interpretation of the Raman spectrum of  $\text{MoS}_2$ .

### 2.B.2. Transmission Electron Microscopy

Standard Bright Field Transmission Electron Microscopy (TEM) can be used to estimate the length and width of the flake [46, 63]. High Resolution TEM (HRTEM) can be used to identify single layers and estimate the number of layers of few-layer flakes. Analysis of the intensity profile of the HRTEM micrographs for single layer  $\text{MoS}_2$  reported a difference between the intensity peaks corresponding to the two neighboring Mo and S atoms. The intensity ratio has been estimated to be 1.15 for single layer  $\text{MoS}_2$ . Such an intensity difference has been reported for very low odd number of layers, with the effect being less evident with increasing number of layers. On the other hand, no difference be-

tween the intensity peak corresponding to neighboring atoms has been reported for a MoS<sub>2</sub> flake with an even number of layers, because of the evenly repeated ABAB stacking sequence of MoS<sub>2</sub> layers [46].

## 2.C. Integration Schemes

There are numerous platforms for integrating few-layer MoS<sub>2</sub> flakes with standard optical components or substrates to form saturable absorber devices, depending on the technique used to process the flakes.

Solution-processed dispersion of few-layer MoS<sub>2</sub> flakes have been integrated into saturable absorber devices by printing or coating onto substrates including optical components such as fiber facets [48, 49, 64–69], transfer of filtered films [46, 70], or by blending with polymers to produce free-standing composites [47, 71–75], similar to integration techniques employed for LPE graphene flakes [15]. Additionally, mechanically exfoliated few-layer MoS<sub>2</sub> flakes can be integrated in similar ways if the exfoliated flakes are dispersed in a solvent [76]. A widely used technique to form a flexible and free-standing SA device, which can be sandwiched between two fiber patchcords in a fiber laser, is to embed few-layer MoS<sub>2</sub> flakes in a polyvinyl alcohol (PVA) polymer film [47, 71–75]. Polymeric materials are an ideal choice of platform to integrate nanomaterials into photonic systems as they are easily manipulated by methods such as embossing, stamping and etching and generally have a low-cost room-temperature fabrication process [15]. However, thermal damage of the polymer can limit their use in high-power fiber and bulk lasers. To circumvent this, few-layer MoS<sub>2</sub> flakes can be directly deposited on a fiber facet by optically-driven deposition from an LPE dispersion [66] or spin-coated onto quartz [66] or BK7 glass [69]. Another integration strategy, which increases the interaction length between light and MoS<sub>2</sub> is to deposit the few-layer MoS<sub>2</sub> dispersion along a microfiber [48, 49] or side-polished fiber [76], causing the SA to interact with the evanescent optical field.

CVD few-layer MoS<sub>2</sub> is typically grown on Si/SiO<sub>2</sub> or sapphire [77]. Integration of such MoS<sub>2</sub> flakes to form SA devices requires flake transferring and placement techniques to move flakes to a desired photonic substrate [38–40]. PLD fabricated MoS<sub>2</sub> flakes require a similar transfer technique, or alternatively, the desired substrate can be used directly in the PLD process [42]. For flake transfer, a polymer such as polymethyl methacrylate (PMMA) is generally spin-coated onto the MoS<sub>2</sub> as-grown film [38, 40]. The growth-substrate is etched (for example with hydrofluoric acid [40, 77] or potassium hydroxide [40, 78]) to lift off the polymer-MoS<sub>2</sub> film, which can then be rinsed and transferred to the new substrate. Finally, the polymer layer is dissolved, leaving the MoS<sub>2</sub> film on the substrate [38–40]. This approach has been used for transferring few-layer MoS<sub>2</sub> films directly onto a fiber connector [77, 79] and for exploiting an evanescent field interaction by de-

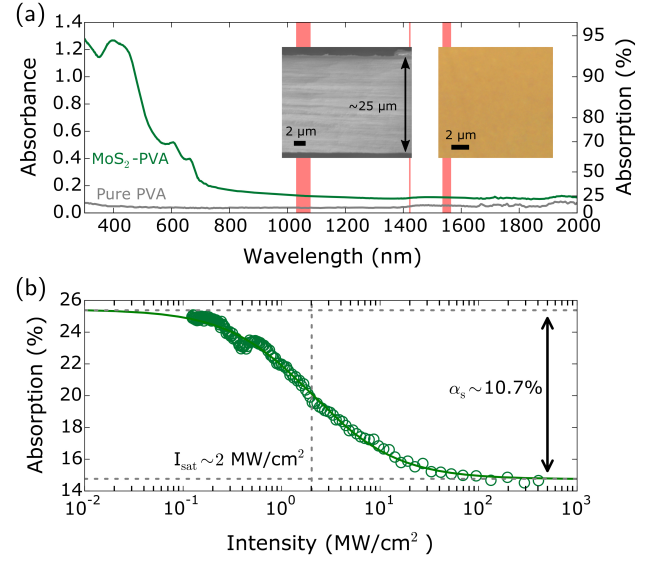


Fig. 2. Optical properties of few-layer MoS<sub>2</sub>-PVA composite (after [73]): (a) linear absorption, compared to pure PVA (red highlighted regions correspond to wavelengths at which MoS<sub>2</sub>-based pulsed lasers have been reported); insets show SEM (left) and optical micrograph (right), confirming the absence of large ( $>1 \mu\text{m}$ ) voids or aggregates; (b) nonlinear absorption of composite film at 1565 nm (0.8 eV).

positing CVD-grown MoS<sub>2</sub> on a side-polished fiber [78].

## 2.D. Few-Layer MoS<sub>2</sub>-PVA Composite SA: A Manufacturing Case Study

Here, we illustrate the fabrication procedure of a few-layer MoS<sub>2</sub>-PVA composite SA device by briefly outlining our typical experimental procedure using LPE. This type of SA has been successfully used for laser pulse generation, continuously tunable within the ranges 1030–1070 nm [72] and 1535–1565 nm [73].

First, MoS<sub>2</sub> powder (120 mg) is mixed with 90 mg of sodium deoxycholate (SDC) bile salt in 10 mL of deionized water for ultrasonication ( $\sim 2$  hr) at a constant temperature of  $\sim 5^\circ\text{C}$ . The thick unexfoliated bulk MoS<sub>2</sub> flakes are sedimented via ultracentrifugation (4200g), enabling the top 80% of the dispersion to be collected that is enriched in single- and few-layer flakes.

The absorption spectrum of this dispersion, diluted to 10 vol% is shown in Fig. 1(b). The four observed peaks, at  $\sim 665$  nm,  $\sim 605$  nm,  $\sim 440$  nm and  $\sim 395$  nm, are termed A, B, C and D according to standard nomenclature [20], and result from excitonic transitions (A, B) [80, 81], and transitions between higher density of state regions of the MoS<sub>2</sub> band-structure (C, D) [80, 81].

Raman spectroscopy of the sample shows the relative position of two peaks close to  $400 \text{ cm}^{-1}$  in the spectrum, corresponding to the in-plane ( $E_{2g}^1$ ) and out of plane ( $A_{1g}$ ) vibration modes, and can be used to estimate the number of layers in a sample [57, 62, 82], since the separation between the peak positions ( $\Delta w$ )

increases from  $18.7 \text{ cm}^{-1}$  to  $25 \text{ cm}^{-1}$  between monolayer and 6-layer samples [57], reaching  $25.5 \text{ cm}^{-1}$  for bulk  $\text{MoS}_2$  [57, 82]. The spectra for the dispersed  $\text{MoS}_2$  flakes, and for bulk  $\text{MoS}_2$  are shown in Fig. 1(c). For the dispersed  $\text{MoS}_2$  flakes,  $\Delta\omega$  is  $(24.62 \pm 0.02) \text{ cm}^{-1}$ , compared with  $(25.29 \pm 0.03) \text{ cm}^{-1}$  for bulk  $\text{MoS}_2$ , confirming the presence of few-layer  $\text{MoS}_2$  flakes with estimated 4-6 layer thickness.

Atomic force microscopy (AFM) allows measurement of the distribution of flake thicknesses [Fig. 1(d)], revealing that  $\sim 60\%$  of the flakes have thickness 2-4 nm, corresponding to 4-6 layers (assuming  $\sim 1 \text{ nm}$  measured thickness for a monolayer flake, and  $\sim 0.7 \text{ nm}$  increase for each subsequent layer [57]), in agreement with the Raman spectroscopy measurements. The average flake dimensions, measured using scanning transmission electron microscopy, are  $(220 \pm 20) \text{ nm}$  by  $(110 \pm 10) \text{ nm}$ .

The composite SA device is prepared by mixing 4 mL of  $\text{MoS}_2$  dispersion with 2 mL of 15 wt% aqueous PVA solution, which is dried in air to form a  $\sim 25 \mu\text{m}$  thick free-standing polymer composite film. The lack of significant shift in the Raman peak positions between the LPE  $\text{MoS}_2$  and LPE  $\text{MoS}_2$ -PVA [Fig. 1(c)] confirms that the  $\text{MoS}_2$  structure is unaffected by its inclusion in the composite. Optical microscopy and scanning electron microscopy (SEM) [Fig. 2(a) inset] are used to verify the absence of large ( $>1 \mu\text{m}$ ) aggregates in the film which could otherwise lead to scattering losses [83] and confirms a uniform distribution of the flakes throughout the composite film. The linear absorption spectrum of the composite is measured, along with that of a pure PVA film of the same thickness, showing a measurable difference in the absorption spectra [Fig. 2(a)], even at photon energies below the known material bandgap of few-layer  $\text{MoS}_2$ , as discussed in Section 3.A.

### 3. Photonic Applications

The unique optical and electronic properties of mono- and few-layer  $\text{MoS}_2$ , and the potential for its large-scale manufacture through solution processing techniques indicate that it could be a suitable platform for the development of photonic devices. A strong second-order nonlinearity,  $|\chi^2| \sim 10^{-7} \text{ m/V}$  [84], (from single and odd-numbered layers of the crystal due to inversion asymmetry) and a high third-order electrical susceptibility,  $|\chi^3| \sim 10^{-19} \text{ m}^2/\text{V}^2$  [85] has been measured, as well as an ultrafast ( $<100 \text{ fs}$ ) relaxation time [25]. This highlights the nanomaterial's potential in nonlinear and ultrafast optical applications, including second- [84, 86] and third-harmonic [85] generation, and as a wideband ultrafast saturable absorber [25]. Additionally, with a direct bandgap of 1.8 eV in monolayer form, the material exhibits a strong visible photo- and electroluminescence [34, 87], opening possibilities for applications including photodetectors, and light-emitting diodes.

With a focus on short-pulse laser technology, in the forthcoming sections we discuss the nonlinear optical properties of  $\text{MoS}_2$  and collate complete tables of saturable absorber devices and pulsed laser demonstrations

that utilize the material to date, before briefly considering the disruptive impact this exciting 2D material has had on other photonic technologies. For a detailed review of the nano- and optoelectronic properties and applications of  $\text{MoS}_2$  that are outside the scope of this article, we refer to Ref. [21].

#### 3.A. Nonlinear Optical Properties

Saturable absorbers are devices with a nonlinear optical absorption profile such that their transmission increases (absorption decreases) with increasing incident light intensity [1]. In semiconductor materials, saturable absorption manifests from the excitation of electrons from the valence band to the conduction band under strong illumination by a source of sufficient photon-energy, leaving the upper states filled and the material unable to absorb further photons according to the Pauli exclusion principle [1, 8]. It should be noted that this mechanism is distinct from graphene that, as a semimetal with no bandgap and exhibiting a linear dispersion of electrons around the Dirac point, generates an electron-hole pair for all incident photons, and saturation follows by rapid thermalization of electron states and Pauli blocking [16].

Nonlinear optical absorption of materials can be measured using two common techniques: open-aperture Z-scan [88] and I-scan (often referred to as the balanced twin-detector technique) [89, 90]. In a Z-scan setup, the sample is swept through the focal plane of a focused train of short optical pulses and the transmission is recorded as a function of position (often in addition to a reference signal for normalization). The spatial position of the sample is mapped to an intensity, allowing continuous control of the incident intensity for a constant input power. To perform an I-scan measurement, which benefits from the option of a fully-fiber integrated setup, a variable average-power pulsed source is split into a test and reference arm, each terminated at two separate detectors, allowing calibration and characterization of the samples nonlinear optical response as a function of a variable input power.

A variety of models have been developed to describe the nonlinear saturable absorption behavior of materials [25, 91]. The absorption,  $\alpha$  as a function of incident light intensity,  $I$  can be expressed simply as:

$$\alpha(I) = \alpha_0 + \alpha_{\text{NL}}I \quad (1)$$

where  $\alpha_0$  and  $\alpha_{\text{NL}}$  are the linear and nonlinear absorption coefficients, respectively. For practical SA devices, a phenomenological model based on the assumption of a two-level system [91], is widely adopted. By using the model to fit to experimentally measured data from I- and Z-scan setups, device parameters can be extracted, and used as a performance comparison metric. This model [91], which assumes an instantaneous material response, has also been extended to account for reverse saturable absorption (RSA) effects (where increased absorption is observed under increased incident intensity), a phenomenon encountered in some nanomaterial-based

photonic devices [25, 55]. If a saturable absorber device in a laser cavity exhibits RSA in addition to SA, the pulse-shaping dynamics can be modified. Depending on the strength and threshold of RSA, it has been reported to suppress Q-switching and also to limit the achievable pulse energies [92]. The augmented model takes the form:

$$\alpha(I) = \frac{\alpha_s}{1 + \frac{I}{I_s}} + \alpha_{ns} + \beta I \quad (2)$$

where  $\alpha_s$  and  $\alpha_{ns}$  are the saturable (i.e. modulation depth) and nonsaturable device loss, respectively;  $I_s$  is the saturation intensity – the intensity which reduces the device absorption by half of the maximum saturable loss; and  $\beta$  is an effective RSA coefficient. The nonlinear absorption profile for our case-study few-layer MoS<sub>2</sub> SA (Section 2.D) is shown in Fig. 2(b), obtained by a Z-scan experiment at 1565 nm with 750 fs pulses at 17.8 MHz repetition rate. The SA parameters are determined by fitting the data with Eqn. (2):  $I_{sat} = 2.0 \text{ MW cm}^{-2}$ ,  $\alpha_s = 10.7\%$ ,  $\alpha_{ns} = 14.7\%$  and RSA is negligible.

Table 1 summarizes nonlinear absorption measurements conducted on few-layer MoS<sub>2</sub> in the literature to date: Table 1(a) describes the properties of few-layer MoS<sub>2</sub> dispersion from solution-processing approaches and Table 1(b) presents the parameters for demonstrated MoS<sub>2</sub>-based SA devices. The first nonlinear measurements were performed by Wang *et al.* [25] using a Z-scan setup (with an 800 nm source of 100 fs pulses at 1 kHz repetition frequency) and LPE-fabricated few-layer MoS<sub>2</sub> flakes in N-methylpyrrolidone (NMP), with average flake thickness of 5-6 layers and lateral dimensions <200 nm. Saturable absorption was observed due to carrier excitation through single photon absorption at 800 nm (1.55 eV). However, it was argued that two photon absorption (TPA) could also be observed due to a small fraction of monolayer flakes with ~1.8 eV energy gap, greater than the incident photon energy. The saturation intensity was measured as  $I_s = 413 \text{ GW cm}^{-2}$  and the nonlinear absorption was  $-4.6 \times 10^{-3} \text{ cm GW}^{-1}$ . The nonlinear absorption coefficient is also occasionally referred to as the TPA coefficient, so a negative  $\alpha_{NL}$  refers to SA. Using the same experimental setup and a graphene dispersion, it was concluded that MoS<sub>2</sub> possesses a larger SA response in its resonant band [25]. The MoS<sub>2</sub> intraband relaxation time was also computed as ~30 fs [25] and interband transitions have been reported on picosecond timescales [94]. The two timescales suggest ideal SA behavior: the longer relaxation route aids pulsed-laser self-starting, whereas the ultrafast relaxation enables ultrashort pulse generation, similar to the two timescales exhibited by graphene [16].

Other works have verified that the average number of layers in MoS<sub>2</sub> flakes can determine whether the nonlinear response is in the SA or RSA regime. Cyclohexylpyrrolidone (CHP) dispersions – containing 15 layer-thick and 6 layer-thick flakes – were characterized using Z-scan at 1030 nm (1.20 eV, corresponding to the

bulk MoS<sub>2</sub> bandgap) [93]. The dispersion with an average of 15-layer flakes exhibited SA, corresponding to single-photon absorption, but the 6-layer flake dispersion showed TPA, explained by the increased bandgap energy of few-layer flakes [93]. Strong SA has also been widely observed for excitation with photon energies exceeding the monolayer bandgap – e.g. at 532 nm (2.33 eV) [55, 93].

A behavioral-dependence on the lateral and longitudinal flake size was also reported for flakes with constant thickness of ~4.9 nm (<7 layers) [55]. By varying the centrifugation speed during the LPE process, it is possible to vary the resulting flake size. Zhou *et al.* [55] found that Z-scans performed on larger flakes (>100 nm lateral/longitudinal lengths) at 532 nm exhibited SA behavior, as expected for above-bandgap excitation, but dispersions containing smaller flakes (with 50-60 nm average dimensions) exhibited RSA. Using transient absorption spectroscopy, they showed that excited state absorption (ESA) was the responsible mechanism, proposing that the difference in behavior for large and small flakes was due to an increased proportion of edge defects in smaller flakes. It was proposed that unsaturated edges could create localized edge states within the bandgap, assisting the excitation of electrons into the conduction band. However, edge states can be quenched at higher powers leading to RSA behavior [55]. In graphene, due to the zero bandgap, edge states are not involved in the absorption mechanism [55].

A transition from SA to RSA behavior has also been reported with increasing incident intensity by Ouyang *et al.* [95], at 532 nm for 100-200 nm sized flakes with <10 nm thickness (<14 layers) deposited on quartz (importantly, the process was reversible, indicating that the sample was not suffering photo-damage at higher energies). Their analysis showed that ESA played a dominant role in the process [95]. Zhang *et al.* [66] made similar observations of a power-dependent transition from SA to RSA behavior for intercalated 1-3 layer MoS<sub>2</sub> flakes in an IPA dispersion, which was attributed to nonlinear scattering from the formation of microbubbles around the nanomaterial in the host dispersion at high intensities [66].

As well as studies of the fundamental material properties, manufactured SA devices, based on a variety of integration schemes, have also been characterized and used in short-pulse lasers. To date, all MoS<sub>2</sub>-based pulsed lasers have operated at wavelengths longer than 1030 nm, perhaps linked to greater availability of gain media (especially in fiber) for such wavelength regions. We note that this corresponds to photon energies lower than the material bandgap for monolayer, few-layer, and even bulk MoS<sub>2</sub>. For a perfect crystal, absorption of a single photon with an energy lower than transitions at the fundamental energy gap (leading to the excitation of carriers) is forbidden [96, 97].

While multiphoton absorption (including TPA) can occur, this would yield optical limiting behavior rather

Fabrication Method	Dispersed In	MoS <sub>2</sub> # Layers	Flake Size Lateral Size (nm)	Nonlinear Z/I	Characterization $\lambda$	Setup $t$	$f_{\text{rep}}$	$I_s$ (GW cm <sup>-2</sup> )	$\alpha_0$ (cm <sup>-1</sup> )	$\alpha_{\text{NL}}$ (cm GW <sup>-1</sup> )	Ref.
SP-LPE	NMP	5-6	<200	Z	800 nm	100 fs	1 kHz	413	2.37	$-4.60 \times 10^{-3}$	[25]
		NVP	5-6	Z	800 nm	100 fs	1 kHz	833	1.66	$-1.78 \times 10^{-3}$	[25]
		CHP	5-6	Z	800 nm	100 fs	1 kHz	405	2.85	$-5.80 \times 10^{-3}$	[25]
	Ethanol/H <sub>2</sub> O	~15	-	Z	515 nm	340 fs	1 kHz	58	25.34	-0.357	[93]
		~15	-	Z	532 nm	100 ps	10 kHz	1.13	25.7	-26.2	[93]
		~15	-	Z	800 nm	100 fs	1 kHz	381	11.2	$-2.42 \times 10^{-2}$	[93]
		~15	-	Z	1030 nm	340 fs	1 kHz	114	11.8	$-9.17 \times 10^{-2}$	[93]
		~6	-	Z	1030 nm	340 fs	1 kHz	-	0.034	$+8.0 \times 10^{-5}$ (RSA)	[93]
		~15	-	Z	1064 nm	100 ps	10 kHz	2.1	11.6	-5.5	[93]
	IPA	<7	<500 nm	Z	532 nm	19 ps	10 Hz	~1	-	>7% SA *	[55]
		<7	~100 nm	Z	532 nm	19 ps	10 Hz	~1	-	>5% SA *	[55]
		<7	~50-60 nm	Z	532 nm	19 ps	10 Hz	~1	-	(RSA)	[55]
	IPA	1-3	-	Z	400 nm	100 fs	1 kHz	136	-	10% SA *	[66]
		1-3	-	Z	800 nm	100 fs	1 kHz	280	-	34% SA *	[66]
		1-3	-	I	800 nm	100 fs	1 kHz	338	-	33% SA *	[66]

Fabrication Method	Integration Platform	MoS <sub>2</sub> # Layers	Flake Size Lateral Size (nm)	Nonlinear Z/I	Characterization $\lambda$	Setup $t$	$f_{\text{rep}}$	$I_s$ (MW cm <sup>-2</sup> )	Modulation Depth, $\alpha_s$ (%)	Unsaturable Loss, $\alpha_{\text{ns}}$ (%)	Ref.
SP-LPE	PVA composite	3-4	-	I	1560 nm	250 fs	22.2 MHz	10	2	48.5	[74]
		4-5	~220	Z	1065 nm	500 fs	26.4 MHz	1.6	6.3	18.0	[72]
		4-5	~220	Z	1565 nm	750 fs	17.8 MHz	2.0	10.7	14.7	[73]
		~3	-	I	1566 nm	212 fs	22.0 MHz	13	1.6	54.8	[75]
SP-I	BK7 glass	~3	-	I	1560 nm	250 fs	22.0 MHz	13	-	-	[69]
		1-3	-	I	1041 nm	~ ps	6.54 MHz	-	10.5	78.0	[49]
		4-5	-	I	1554 nm	500 fs	26.0 MHz	-	2.8	57.3	[48]
		4-5	-	I	1554 nm	500 fs	26.0 MHz	34	4.3	24	[47]
CVD	Quartz	1-3	-	Z	800 nm	100 fs	1 kHz	1850	15.9	-	[66]
		4-5	-	I	1550 nm	250 fs	20.0 MHz	0.34	35.4	34.1	[77]
		4-5	-	I	1550 nm	250 fs	20.0 MHz	0.43	33.2	35	[79]
		<10	100-400	I	1563 nm	800 fs	-	>100	>2.5	<70	[78]
ME	Side-polished fiber	1-8	-	I	1552 nm	-	-	-	>2.1	<90	[76]
PLD	Fiber facet	~30	-	Z	1060 nm	40 ps	-	2450	27	-	[42]
HTG	Quartz	3-10	-	I	1030 nm	-	-	18	10.7	39	[41]

Table 1. Nonlinear absorption parameters of (a) few-layer MoS<sub>2</sub> dispersion and (b) few-layer MoS<sub>2</sub> saturable absorber devices. Where distributions of MoS<sub>2</sub> flake sizes were reported, we quote the average flake dimensions. SP-I - solution-processed using intercalation, SP-LPE solution-processed using liquid phase exfoliation, CVD - chemical vapor deposition, ME - mechanical exfoliation, PLD - pulsed laser deposition, HTG - hydrothermal growth, NMP - N-methylpyrrolidone, NVP - N-vinylpyrrolidone, CHP - cyclohexylpyrrolidone, IPA - isopropyl alcohol; Nonlinear characterization setup parameters: Z/I - Z-/I-Scan,  $\lambda$  - wavelength,  $t$  - pulse duration,  $f_{\text{rep}}$  - pulse repetition rate. \* indicates that a  $\alpha_{\text{NL}}$  value was not given (using the models adopted in this work) so an absolute modulation depth has been estimated instead which is dependent on the sample length.

than SA [96, 97], and hence a question persists: how can few-layer MoS<sub>2</sub> devices behave as SAs at photon energies lower than the material bandgap? In fact, few-layer MoS<sub>2</sub> is not an infinite, perfect crystal; boundary effects, edges and defects will contribute to a modification of the absorption spectrum [42, 55, 96, 98–101]. Wang *et al.* [42] proposed an explanation based on atomic defects, following theoretical studies of the bandgap behavior using the plane-wave basis Vienna ab initio simulation package (VASP). The introduction of both Mo and S defects can reduce the bandgap, although an excess of Mo defects leads to metallic behavior with no SA effects, whereas S defects maintain the semiconductor behavior and can reduce the bandgap to 0.08 eV (supporting the generation of photoexcited carriers up to wavelengths as long as 15.4  $\mu\text{m}$ , and consequently SA by Pauli blocking).

Recently, we proposed a complementary explanation based on edge-state absorption [72], supported by early studies on few-layer MoS<sub>2</sub>. Specifically, Roxlo *et al.* [98–100] performed photothermal deflection spectroscopy (PDS) measurements to characterize the absorption

(noting PDS is unaffected by scattering) of different sizes of few-layer MoS<sub>2</sub> flakes at photon energies above and below the bandgap. They found very similar absorption spectra for photoexcitation at wavelengths corresponding to energies higher than the material bandgap, but at sub-bandgap wavelength-equivalent energies, small flakes of few-layer MoS<sub>2</sub> ( $\sim 1 \mu\text{m}$  across) showed up to two orders of magnitude greater absorption than a single crystal. Texturing of single crystals has also been shown to increase sub-bandgap absorption by a factor of ten [99, 100]. Smaller or textured flakes possess a larger edge to surface-area ratio, suggesting a greater contribution to the absorption spectra from edge states that form quasi-energy levels within the forbidden energy gap of the pristine crystal band structure [96, 98–100]. The appearance of edge sites in the bandgap could explain observations of absorption at photon energies lower than the single MoS<sub>2</sub> crystal bandgap that, when saturated at high intensities by Pauli blocking, lead to SA behavior [72]. This mechanism for SA is supported by reports of mode-locking using defect in-bandgap states in other nonlinear crystals [102, 103], in addition to recent



reports of enhanced nonlinear optical processes at few-layer MoS<sub>2</sub> flake edges [101].

The nonlinear sub-bandgap absorption of few-layer MoS<sub>2</sub> SA devices, designed specifically for use in laser cavities, has been measured at  $\sim 1060$  nm [41, 42, 49, 72] and  $\sim 1550$  nm [47, 73–79]. A wide range of parameters have been reported (see Table 1) with: saturation intensities from  $<1$  MW cm<sup>-2</sup> [77, 79] to 2.45 GW cm<sup>-2</sup> [42]; modulation depths between 1.6% [75] and 35.4% [77]; and nonsaturable loss values from 14.7% [73] to  $\sim 90\%$  [76]. Wide variation is even observed between devices produced using the same few-layer MoS<sub>2</sub> flake fabrication methods and integration platforms. Since the ideal SA parameters depend on the type of laser being designed and whether mode-locked or Q-switched operation is desired [1], the range of parameters offered by MoS<sub>2</sub> SAs and ability to engineer their performance is beneficial. Devices containing a variety of average MoS<sub>2</sub> flake thicknesses, from  $\sim 3$  [49, 66, 69, 74, 75] to  $\sim 30$  [42] layers have been demonstrated as SAs at numerous wavelengths which correspond to sub-bandgap absorption (incident photon energy less than the bandgap). Such wideband SA behavior could be attributed to a distribution of edge states within the bandgap [72]. However, the non-saturable loss of devices to date is high (often  $>20\%$ ), which could limit the application of such devices in lower gain systems, including diode-pumped solid-state lasers [104].

### 3.B. MoS<sub>2</sub>-based Short-pulse Lasers

Short-pulse lasers can loosely be categorized as coherent light sources generating pulses of the order of several microseconds, nanoseconds or even few-femtoseconds in duration (where the latter group is typically termed ultrafast lasers). The pulsed-mode of a laser can be initiated by the inclusion of a saturable absorber to act as a passive optical switch. Depending on the parameters of the saturable absorber, such as its strength of absorption (or modulation depth) or characteristic recovery time, and the design of the laser cavity, distinct regimes of operation exist that have qualitatively and quantitatively different characteristics [1, 2].

In Q-switched lasers, the saturable absorber modulates the laser cavity Q-factor: when the absorber is unsaturated the Q-factor is low, thus energy in the gain medium accumulates; as the intra-cavity energy increases the absorber saturates, rapidly increasing the Q-factor and the laser pulse power, allowing efficient extraction of energy stored in the gain medium in a single giant pulse. After the Q-switch the absorber and the gain recover. Q-switched laser pulses are typically characterized by [1, 2]:

- high-energy ( $\mu\text{J}$ – $\text{mJ}$ );
- low repetition frequency (kHz);
- $\mu\text{s}$ – $\text{ns}$  duration.

Consequently, Q-switched lasers target applications such as materials processing, where energetic pulses are required to remove or ablate material [4]. In a distinct regime, known as mode-locking, the saturable absorber applies a modulation, with a periodicity equal to the cavity round-trip time, coupling longitudinal cavity modes and locking their phases, generating a train of pulses. Mode-locked laser pulses are typically characterized by [1, 2]:

- lower-energy compared to Q-switched lasers ( $\text{pJ}$ – $\mu\text{J}$ );
- higher-repetition rate (MHz–GHz);
- shorter duration (ps–fs).

Mode-locked lasers are suitable for high-peak power, low-average power, time-resolved applications, such as optical metrology and biophotonic imaging [3]. In both regimes the properties of the SA play a central role in defining laser operation, thus new materials for SA devices that exhibit wideband intensity dependent absorption with a high modulation depth, ultrafast response and low nonsaturable loss, in addition to environmental robustness are in great demand.

Since the successful exfoliation and characterization of the optical properties of 2D MoS<sub>2</sub>, there have been a number of demonstrations of short-pulse laser operation utilizing the semiconducting nanomaterial; similar to graphene, heralded for its potential for broadband, ultrafast switching operation. Table 2 summarizes the parameters and properties of lasers based on MoS<sub>2</sub> SAs to date. The majority of pulsed lasers using MoS<sub>2</sub> have employed fiber gain media [47–49, 66, 71–79], although MoS<sub>2</sub> SAs have also been successfully deployed in bulk lasers [41, 42, 69]. However, it should be noted that the numerous advantages of fiber lasers such as high gain, their alignment-free, monolithic architecture, and efficient heat dissipation relax the requirements of the SA. Fiber systems can typically tolerate higher nonsaturable losses that are prohibitive in bulk lasers [67].

The first short-pulse laser using a few-layer MoS<sub>2</sub> SA was a bulk Q-switched cavity, reported by Wang *et al.* [42], followed by the first demonstration of a MoS<sub>2</sub>-based Q-switched fiber laser by Woodward *et al.* [71]. Since then, numerous other few-layer MoS<sub>2</sub>-based Q-switched lasers have been reported, operating over a wide wavelength range, including operation at:  $\sim 1060$  nm [41, 42, 69, 71, 72, 75],  $1420$  nm [42],  $\sim 1550$  nm [74–76, 79],  $2032$  nm [75] and  $2100$  nm [42] (Table 2). Demonstrations also include tunable operation over the Yb gain band ( $1030$ – $1070$  nm) [72] and Er gain band ( $1520$ – $1568$ ) [74], further confirming the wideband operation of few-layer MoS<sub>2</sub> SAs. A typical design for a Q-switched fiber laser is shown in Fig. 3(a) (after [72]), in addition to the measured output properties [Fig. 3(b,c,d)] showing a  $74$  kHz pulse train,  $2.88$   $\mu\text{s}$  duration pulse and representative laser spectra from within the tunable operating range. Bulk Q-switched



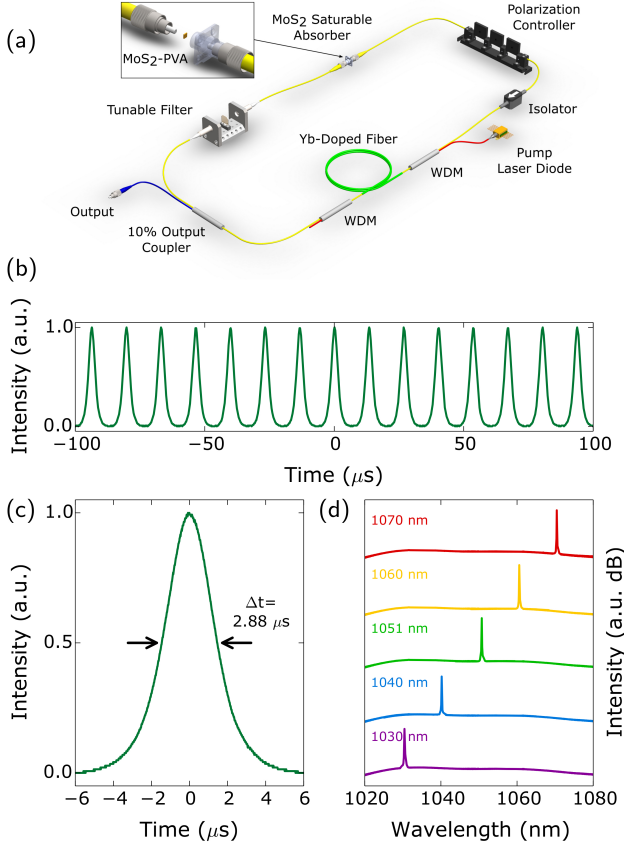


Fig. 3. Tunable MoS<sub>2</sub> Q-switched fiber laser (after [72]): (a) cavity schematic; (b) output 74 kHz pulse train; (c) profile of single pulse; (d) various spectra at wavelengths within the continuous tuning range of 1030-1070 nm.

lasers have generated pulses at much greater output powers ( $>200$  mW) than their fiber counterparts (typically  $<10$  mW), which suggests a high damage threshold of SAs employing few-layer MoS<sub>2</sub> on glass substrates, although the exact intensity on the device was unreported. The highest average output power of 260 mW [69], corresponding to a pulse energy of  $1.1 \mu\text{J}$ , suggests such sources could be applied in medical therapeutics or for material processing [4].

The first mode-locked laser using a MoS<sub>2</sub> SA was reported by Zhang *et al.*, based on a Yb: fiber laser [66]. Subsequently, numerous other MoS<sub>2</sub> mode-locked fiber lasers have been reported within both Yb and Er gain bands, with a wide range of output powers, pulse durations and repetition rates. All MoS<sub>2</sub> mode-locked lasers to date have employed unidirectional ring cavity designs; the highest reported output power is 9.3 mW, corresponding to a maximum pulse energy of 1.4 nJ. The highest peak power generated to date is  $\sim 420$  W [77], and the highest repetition frequency – mode-locking at the 369th cavity harmonic – is 2.5 GHz [48]. Pulse generation in both the net-anomalous soliton regime and all-normal dispersion regimes have been observed, with the

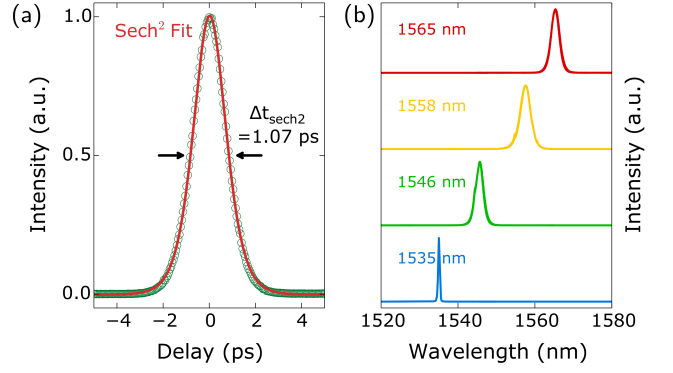


Fig. 4. Tunable MoS<sub>2</sub> mode-locked fiber laser characteristics (after [73]): (a) typical autocorrelation trace; (b) various spectra at wavelengths within the continuous tuning range of 1535–1565 nm. Spectral narrowing towards shorter wavelengths is due to overlapping with the fall-off of the amplifier gain bandwidth (and resulted in longer pulses [73])

shortest pulse duration recorded as 710 fs [47]. A continuously tunable mode-locked laser from 1535–1565 nm, producing picosecond pulses (Fig. 4), has also been reported, highlighting the broadband operation of MoS<sub>2</sub>-based SAs [73]. A bulk mode-locked laser employing few-layer MoS<sub>2</sub> has yet to be demonstrated, possibly due to the high non-saturable loss of current MoS<sub>2</sub> SAs, which could preferentially support Q-switched operation over mode-locking [1, 2], although with further improvements to fabrication and integration procedures to produce low-loss SA devices, we expect that this will soon be possible.

### 3.C. Other Devices

The scope of this article has been restricted to a discussion of mono- and few-layer MoS<sub>2</sub>-based devices from the perspective of short-pulse laser technology, using the devices as saturable absorbers to promote pulsed operation, either by the mechanisms of Q-switching or mode-locking. In this section we briefly consider other photonic applications of 2D MoS<sub>2</sub>.

Distinct from the semimetallic nature of graphene, the direct gap semiconducting properties of monolayer MoS<sub>2</sub>, which efficiently absorbs and emits photons via transitions at the fundamental energy gap [23], supports opportunities for the optoelectronic and photonic application of 2D materials, not previously exploited, including: nanoscale electro-optic modulators at visible frequencies [105]; photodetectors with high responsivity [61, 106, 107]; light-emitting diodes [87]; and solar-cells [108, 109]. Similarly, a lack of inversion symmetry in single, and odd-layers of MoS<sub>2</sub> differentiates prospective applications compared to those of graphene; not least giving rise to a finite second-order optical nonlinearity ( $\chi^2 \neq 0$ ), leading to observations of intense second harmonic generation from monolayer crystals of the material [84, 101, 110], and the ability to optically control

Laser Type	Few-Layer MoS <sub>2</sub> Fabrication Method	Integration Platform	# Layers in MoS <sub>2</sub> Flakes	$\lambda$ (nm)	Laser Properties			Ref.
Mode-Locked								
Yb:Fiber	SP-I	Microfiber	1-3	1043	656 ps	6.7 MHz	2.4	[49]
		Fiber facet	1-3	1054	800 ps	6.6 MHz	9.3	[66]
Er:Fiber	CVD	Fiber facet	4-5	1569	1.28 ps	8.3 MHz	5.1	[77]
		Side-polished fiber	<10	1568	4.98 ps	26.0 MHz	2.0	[78]
		Side-polished fiber	<10	1568	637 fs	33.5 MHz	-	[78]
		PVA composite	4-5	1535-1565 tunable	~1 ps	13.0 MHz	-	[73]
	SP-LPE	PVA composite	4-5	1570	710 fs	12.1 MHz	1.8	[47]
		Microfiber	4-5	1558	3 ps	2.5 GHz	5.4	[48]
Q-Switched								
Yb:Fiber	SP-LPE	PVA composite	4-5	1068	2.7 $\mu$ s	67 kHz	0.5	[71]
		PVA composite	4-5	1030-1070 tunable	2.7 $\mu$ s	89 kHz	10.3	[72]
		PVA composite	~3	1067	10.7 $\mu$ s	13.4 kHz	0.9	[75]
Nd:GdVO <sub>4</sub>	PLD	Quartz	~30	1060	970 ns	732 kHz	227	[42]
Nd:YAlO <sub>3</sub>	SP-LPE	BK7 glass	~3	1080	227 ns	233 kHz	260	[69]
Nd:YGG	PLD	Quartz	~30	1420	729 ns	77 kHz	52	[42]
Yb:YAG	HTG	PVA composite	3-10	1030	12 $\mu$ s	17 kHz	250	[41]
Er:Fiber	SP-LPE	PVA composite	3-4	1520-1568 tunable	5 $\mu$ s	35 kHz	1.5	[74]
		PVA composite	~3	1565	7.5 $\mu$ s	11.9 kHz	1.7	[75]
	CVD	Fiber facet	4-5	1550	1.6 $\mu$ s	173 kHz	4.7	[79]
		Fiber facet	1-8	1563	3.9 $\mu$ s	41 kHz	3.5	[76]
	ME	Fiber facet	1-8	1563	3.9 $\mu$ s	41 kHz	3.5	[76]
Tm:Fiber	SP-LPE	PVA composite	~3	2032	2.06 $\mu$ s	38.4 kHz	47.3	[75]
Tm:Ho:YGG	PLD	Quartz	~30	2100	410 ns	149 kHz	206	[42]

Table 2. Pulsed lasers with few-layer MoS<sub>2</sub> SAs. Where ranges of parameters were reported for Q-switched lasers due the power-dependent repetition rate and pulse duration, we quote the properties at the maximum power. SP-I - solution-processed using intercalation, SP-LPE solution-processed using liquid phase exfoliation, CVD - chemical vapor deposition, ME - mechanical exfoliation, PLD - pulsed laser deposition, HTG - hydrothermal growth,  $\lambda$  - operating wavelength,  $t$  - pulse duration,  $f_{\text{rep}}$  - pulse repetition rate,  $P$  - average output power.

the valley polarization state [111, 112], allowing new opportunities in the emergent field of *valleytronics* [113]. Due to a large elastic strain that monolayers of the material can accommodate, bandgap engineering of MoS<sub>2</sub> permits tailoring of its optical properties [114].

The favorable optical properties of MoS<sub>2</sub> can be further enhanced by vertical hybrid heterostructuring, where single-layers form trap-free binary or multilayered devices with graphene (known as G-TMD stacks) [115, 116], or indeed another layered 2D semiconductor from the TMD family of materials (TMD-TMD stacks) [117–119]. Both material systems are receiving considerable attention, from a theoretical and experimental perspective, because of the highly engineerable architecture, due to the dangling-bond-free surfaces of 2D crystals, and the ability to be able to readily form semiconductor junctions with the desired band alignment, due to the library of available 2D materials. In the case of TMD-TMD stacks, similar crystal structure and growth conditions supports synthesis and large-scale fabrication using CVD, while providing another route to modification of the electronic band structure. Among a number of advantages, G-TMDs exploit the high mobility in graphene, leading to fast response times, and the strong visible absorption of MoS<sub>2</sub>, to form devices including photodetectors, exhibiting an ultra-high photo-gain [116].

Despite the fact that TMDs, such as MoS<sub>2</sub> are heralded as exhibiting strong light absorption at energies corresponding to their exciton resonances, due to their atomically-thin nature and consequently short absorption lengths, 2D materials possess weak light-matter interactions in absolute terms [117]. Multilayers offering

stronger absorption mitigate this paradox; however, the benefits of a 2D structure, including strong quantum confinement, can be compromised. This inherently weak optical interaction can potentially be circumvented, or the interaction enhanced, through a unison with plasmonic nanostructures, where the excitation of plasmonic surface modes can achieve a strong change in the optical response of a nearby material layer [117].

#### 4. Conclusion and Outlook

The recent research interest in few-layer MoS<sub>2</sub> has revealed numerous favorable material properties, exploitable for future photonic applications. For short-pulse laser technology, the nonlinear optical properties are of particular interest: few-layer MoS<sub>2</sub> exhibits a broadband nonlinear response, showing both saturable absorption and reverse saturable absorption (Table 1). The nature and strength of the nonlinear response has been found to depend on the layer-count of processed few-layer MoS<sub>2</sub> flakes (i.e. flake thickness) [93], lateral/longitudinal flake dimensions [55], and on the device integration scheme. It is worth noting that many studies to date have considered processing methods producing a distribution of flake dimensions [25, 73]. Flakes of different sizes exhibit distinct characteristics [25, 55, 120]; the dominant device behavior corresponds to the average flake size, suggesting that statistical methods are needed to understand and analyze device performance. This dependence allows the engineering of the optical properties of few-layer MoS<sub>2</sub> devices over a wide range.

The reported wideband behavior of MoS<sub>2</sub> SAs is very promising, enabling one few-layer MoS<sub>2</sub>-based SA device to operate at many different laser wavelengths (Table 2).

At excitation photon energies greater than the material bandgap, the SA mechanism has been explained by single-photon absorption exciting electrons into the conduction band, followed by Pauli blocking [25, 55, 72, 95]. For photon energies lower than the bandgap, TPA and ESA have been reported as absorption mechanisms giving rise to RSA behavior [25]. However, sub-bandgap SA behavior has also been reported [55, 72]. While single-photon absorption is forbidden in a perfect infinite crystal [96], the finite-sized 2D flakes of few-layer MoS<sub>2</sub> possess a high edge to surface area ratio [55, 72]. These defect sites [42] and edge states [72, 99], support absorption of light at wavelengths longer than the wavelength equivalent bandgap energy, and consequently can exhibit SA through Pauli blocking at high intensities [42, 72].

With regards to integration, a wide variety of platforms have been reported using few-layer MoS<sub>2</sub> flakes from a range of processing techniques, including embedding flakes in a PVA-composite, direct deposition on fiber facets, microfibers and side-polished fibers and also deposition on quartz / BK7 glass. These SA devices have been used to Q-switch and mode-lock both bulk and fiber lasers from 1030 nm to 2100 nm, enabling laser pulse generation at kilohertz to gigahertz repetition rates and with few microsecond to sub-picosecond pulse durations. The output powers of MoS<sub>2</sub>-based lasers to date have been modest – typically a few milliwatts for fiber lasers, although extra-cavity amplification and power scaling in master-oscillator power amplifier configurations is expected to lead to higher achievable powers [121]. For fiber lasers, nonlinear effects can limit the maximum achievable peak power [121], although recent progress suggests a route to high pulse energy fiber lasers by using large-mode area fiber [122] and novel all-normal dispersion, long-cavity designs that produce low-repetition rate trains of high-energy giant-chirped pulses, suitable for compact chirped pulse amplification and compression setups [123, 124]. The inclusions of few-layer MoS<sub>2</sub>-based SAs in other laser platforms, such as thin-disk and vertical external-cavity surface-emitting lasers (VECSELs) is also expected, offering greater versatility, and power scalability [125]. However, the high nonsaturable loss of current MoS<sub>2</sub> SAs could present problems for their application in bulk systems – further work is needed to lower this loss while maintaining the high saturable component.

The performance properties of few-layer MoS<sub>2</sub> SAs, such as ultrafast material relaxation time [25], fabrication and integration flexibility [18], and the potential for wideband operation throughout the near-IR [42, 72], are comparable to other nanomaterial-based SAs, including graphene and carbon nanotubes [15, 16, 67]. However, the potential for application of few-layer MoS<sub>2</sub> SAs at visible wavelengths, around the peak of the fundamental exciton resonance [22], offers a tangible advantage over competing technologies. The required tube diameter to achieve strong visible resonant absorption in nanotubes presents fabrication difficulties [15] and the satu-

ration intensity of graphene scales inversely with wavelength [17], which is unfavorable for visible lasers. However, monolayer MoS<sub>2</sub> has a direct 1.80 eV bandgap [22] (equivalent to a wavelength of 689 nm) and the bandgap for few-layer crystals can also correspond to energies in the visible spectral range. Indeed, existing MoS<sub>2</sub> studies have experimentally confirmed saturable absorption at 532 nm [55, 93], paving the way to visible short-pulse lasers using few-layer MoS<sub>2</sub> SA devices.

Finally, we note that MoS<sub>2</sub> is only one material within the family of transition metal dichalcogenides. Numerous studies discussed in this review also considered the nonlinear optical properties of other TMDs, such as MoSe<sub>2</sub> and WS<sub>2</sub>; observing similarly strong SA and RSA responses from these layered materials. The explanations for layer-dependent properties and edge-driven sub-bandgap absorption could apply for other few-layer TMDs, suggesting their application as SAs for short-pulse lasers. Indeed, few-layer tungsten disulfide (WS<sub>2</sub>) SAs are beginning to emerge [126–129]. However, further work is still required to critically evaluate their properties. Additionally, vertical hybrid heterostructuring of TMDs represents a new material system, with promising optical properties that could allow even greater control and engineering of laser pulse sources.

## Acknowledgments

The authors would like to thank J. R. Taylor for fruitful discussions. EJRK and TH acknowledge support from the Royal Academy of Engineering (RAEng).

## References

- [1] O. Svelto, *Principles of Lasers* (Springer, 2010).
- [2] A. E. Siegman, *Lasers* (University Science Books, 1990).
- [3] F. Dausinger, F. Lichtner, and H. Lubatschowski, *Femtosecond Technology for Technical and Medical Applications* (Springer, 2004).
- [4] W. M. Steen and J. Mazumder, *Laser Material Processing* (Springer, 2010).
- [5] B. H. Chapman, E. J. R. Kelleher, K. M. Golant, S. V. Popov, and J. R. Taylor, “Amplification of picosecond pulses and gigahertz signals in bismuth-doped fiber amplifiers,” *Opt. Lett.* **36**, 1446 (2011).
- [6] N. D. Psaila, R. R. Thomson, H. T. Bookey, A. K. Kar, N. Chiodo, R. Osellame, G. Cerullo, A. Jha, and S. Shen, “Er:Yb-doped oxyfluoride silicate glass waveguide amplifier fabricated using femtosecond laser inscription,” *Appl. Phys. Lett.* **90**, 131102 (2007).
- [7] U. Keller, K. J. Weingarten, F. X. Kartner, D. Kopf, B. Braun, I. D. Jung, R. Fluck, C. Honninger, N. Matuschek, J. Aus der Au, “Semiconductor saturable absorber mirrors (SESAMs) for femtosecond to nanosecond pulse generation in solid-state lasers,” *IEEE J. Quant. Electron.* **2**, 435 (1996).
- [8] U. Keller, “Recent developments in compact ultrafast lasers,” *Nature* **424**, 831 (2003).
- [9] K. Tamura, H. A. Haus, and E. P. Ippen, “Self-starting additive pulse mode-locked erbium fibre ring laser,” *Electron. Lett.* **28**, 2226 (1992).

- [10] S. Iijima, "Helical microtubules of graphitic carbon," *Nature* **354**, 56 (1991).
- [11] P. Avouris, M. Freitag, and V. Perebeinos, "Carbon-nanotube photonics and optoelectronics," *Nature Photon.* **2**, 341 (2008).
- [12] K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," *Science* **306**, 666 (2004).
- [13] F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nature Photon.* **4**, 611 (2010).
- [14] S. Set, H. Yaguchi, Y. Tanaka, and M. Jablonski, "Ultrafast fiber pulsed lasers incorporating carbon nanotubes," *IEEE J. Sel. Top. Quantum Electron.* **10**, 137 (2004).
- [15] T. Hasan, Z. Sun, F. Wang, F. Bonaccorso, P. H. Tan, A. G. Rozhin, and A. C. Ferrari, "Nanotube-polymer composites for ultrafast photonics," *Adv. Mater.* **21**, 3874 (2009).
- [16] Z. Sun, T. Hasan, F. Torrisi, D. Popa, G. Privitera, F. Wang, F. Bonaccorso, D. M. Basko, and A. C. Ferrari, "Graphene mode-locked ultrafast laser," *ACS Nano* **4**, 803 (2010).
- [17] Q. Bao, H. Zhang, Y. Wang, Z. Ni, Y. Yan, Z. X. Shen, K. P. Loh, and D. Y. Tang, "Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers," *Adv. Funct. Mater.* **19**, 3077 (2009).
- [18] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," *Nat. Nanotechnol.* **7**, 699 (2012).
- [19] M. Z. Hasan and C. L. Kane, "Colloquium: Topological insulators," *Rev. Mod. Phys.* **82**, 3045 (2010).
- [20] J. A. Wilson and A. Yoffe, "The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties," *Adv. Phys.* **18**, 193 (1969).
- [21] R. Ganatra and Q. Zhang, "Few-layer MoS<sub>2</sub>: a promising layered semiconductor," *ACS Nano* **8**, 4074 (2014).
- [22] R. G. Dickson and L. Pauling, "The crystal structure of molybdenite," *J. Am. Chem. Soc.* **45**, 1466 (1923).
- [23] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, "Emerging photoluminescence in monolayer MoS<sub>2</sub>," *Nano Lett.* **10**, 1271 (2010).
- [24] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS<sub>2</sub> transistors," *Nat. Nanotechnol.* **6**, 147 (2011).
- [25] K. Wang, J. Wang, J. Fan, M. Lotya, A. O'Neill, D. Fox, Y. Feng, X. Zhang, B. Jiang, Q. Zhao, H. Zhang, J. N. Coleman, L. Zhang, and W. J. Blau, "Ultrafast saturable absorption of two-dimensional MoS<sub>2</sub> nanosheets," *ACS Nano* **7**, 9260 (2013).
- [26] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat. Mater.* **6**, 183 (2007).
- [27] R. Frindt and A. Yoffe, "Physical properties of layer structures: optical properties and photoconductivity of thin crystals of molybdenum disulphide," *Proc. R. Soc. Lond. A* **273**, 69 (1963).
- [28] R. F. Frindt, "Optical absorption of a few unit-cell layers of MoS<sub>2</sub>," *Phys. Rev.* **140**, A536 (1965).
- [29] R. F. Frindt, "Single crystals of MoS<sub>2</sub> several molecular layers thick," *J. Appl. Phys.* **37**, 1928 (1966).
- [30] P. Joensen, R. F. Frindt, and S. R. Morrison, "Single-layer MoS<sub>2</sub>," *Mater. Res. Bull.* **21**, 457 (1986).
- [31] F. Bonaccorso and Z. Sun, "Solution processing of graphene, topological insulators and other 2d crystals for ultrafast photonics," *Opt. Mater. Express* **4**, 63 (2014).
- [32] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, and A. C. Ferrari, "Production and processing of graphene and 2d crystals," *Mater. Today* **15**, 564 (2012).
- [33] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, "Two-dimensional atomic crystals," *Proc. Natl. Acad. Sci. U.S.A.* **102**, 10451 (2005).
- [34] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically thin MoS<sub>2</sub>: a new direct-gap semiconductor," *Phys. Rev. Lett.* **105**, 136805 (2010).
- [35] S. Helveg, J. V. Lauritsen, E. Lægsgaard, I. Stensgaard, J. K. Nørskov, B. S. Clausen, H. Topsøe, and F. Besenbacher, "Atomic-scale structure of single-layer MoS<sub>2</sub> nanoclusters," *Phys. Rev. Lett.* **84**, 951 (2000).
- [36] Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, and J. Lou, "Large-area vapor-phase growth and characterization of MoS<sub>2</sub> atomic layers on a SiO<sub>2</sub> substrate," *Small* **8**, 966 (2012).
- [37] Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li, and T.-W. Lin, "Synthesis of large-area MoS<sub>2</sub> atomic layers with chemical vapor deposition," *Adv. Mater.* **24**, 2320 (2012).
- [38] K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi, H. Zhang, C.-S. Lai, and L.-J. Li, "Growth of large-area and highly crystalline MoS<sub>2</sub> thin layers on insulating substrates," *Nano Lett.* **12**, 1538 (2012).
- [39] Y.-H. Lee, L. Yu, H. Wang, W. Fang, X. Ling, Y. Shi, C.-T. Lin, J.-K. Huang, M.-T. Chang, C.-S. Chang, M. Dresselhaus, T. Palacios, L.-J. Li, and J. Kong, "Synthesis and transfer of single-layer transition metal disulfides on diverse surfaces," *Nano Lett.* **13**, 1852 (2013).
- [40] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, and J. Lou, "Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers," *Nat. Mater.* **12**, 754 (2013).
- [41] Y. Zhan, L. Wang, J. Y. Wang, H. W. Li, and Z. H. Yu, "Yb : YAG thin disk laser passively Q-switched by a hydro-thermal grown molybdenum disulfide saturable absorber," *Laser Phys.* **25**, 025901 (2015).
- [42] S. Wang, H. Yu, H. Zhang, A. Wang, M. Zhao, Y. Chen, L. Mei, and J. Wang, "Broadband few-layer MoS<sub>2</sub> saturable absorbers," *Adv. Mater.* **26**, 3538 (2014).
- [43] V. Fominiski, V. Nevolin, R. Romanov, and I. Smurov, "Ion-assisted deposition of MoS<sub>x</sub> films from laser-generated plume under pulsed electric field," *J. Appl. Phys.* **89**, 1449 (2001).
- [44] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, and M. Chhowalla, "Photoluminescence from chemically exfoliated MoS<sub>2</sub>," *Nano Lett.* **11**, 5111 (2011).
- [45] J. Zheng, H. Zhang, S. Dong, Y. Liu, C. T. Nai, H. S. Shin, H. Y. Jeong, B. Liu, and K. P. Loh, "High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide," *Nat. Commun.* **5**, 2995 (2014).

- [46] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grievson, K. Theuvsen, D. W. McComb, P. D. Nellist, and V. Nicolosi, "Two-dimensional nanosheets produced by liquid exfoliation of layered materials," *Science* **331**, 568 (2011).
- [47] H. Liu, A.-P. Luo, F.-Z. Wang, R. Tang, M. Liu, Z.-C. Luo, W.-C. Xu, C.-J. Zhao, and H. Zhang, "Femtosecond pulse erbium-doped fiber laser by a few-layer MoS<sub>2</sub> saturable absorber," *Opt. Lett.* **39**, 4591 (2014).
- [48] M. Liu, X.-W. Zheng, Y.-L. Qi, H. Liu, A.-P. Luo, Z.-C. Luo, W.-C. Xu, C.-J. Zhao, and H. Zhang, "Microfiber-based few-layer MoS<sub>2</sub> saturable absorber for 25 GHz passively harmonic mode-locked fiber laser," *Opt. Express* **22**, 22841 (2014).
- [49] J. Du, Q. Wang, G. Jiang, C. Xu, C. Zhao, Y. Xiang, Y. Chen, S. Wen, and H. Zhang, "Ytterbium-doped fiber laser passively mode locked by few-layer molybdenum disulfide (MoS<sub>2</sub>) saturable absorber functioned with evanescent field interaction," *Sci. Rep.* **4**, 6346 (2014).
- [50] R. Gordon, D. Yang, E. Crozier, D. Jiang, and R. Frindt, "Structures of exfoliated single layers of WS<sub>2</sub>, MoS<sub>2</sub>, and MoSe<sub>2</sub> in aqueous suspension," *Phys. Rev. B* **65**, 125407 (2002).
- [51] M. A. Py and R. R. Haering, "Structural destabilization induced by lithium intercalation in MoS<sub>2</sub> and related compounds," *Can. J. Phys.* **61**, 76 (1983).
- [52] L. Mattheiss, "Band structures of transition-metal-dichalcogenide layer compounds," *Phys. Rev. B* **8**, 3719 (1973).
- [53] J. N. Israelachvili, *Intermolecular and surface forces* (Academic, 2011).
- [54] T. J. Mason, *Sonochemistry* (Oxford, 1999).
- [55] K.-G. Zhou, M. Zhao, M.-J. Chang, Q. Wang, X.-Z. Wu, Y. Song, and H.-L. Zhang, "Size-dependent nonlinear optical properties of atomically thin transition metal dichalcogenide nanosheets," *Small*, DOI: 10.1002/sml.201400541 (posted 18 September 2014, in press).
- [56] Y. Feldman, E. Wasserman, D. Srolovitz, and R. Tenne, "High-rate, gas-phase growth of MoS<sub>2</sub> nested inorganic fullerenes and nanotubes," *Science* **267**, 222 (1995).
- [57] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, "Anomalous lattice vibrations of single- and few-layer MoS<sub>2</sub>," *ACS Nano* **4**, 2695 (2010).
- [58] Y. Zhao, X. Luo, H. Li, J. Zhang, P. T. Araujo, C. K. Gan, J. Wu, H. Zhang, S. Y. Quek, M. S. Dresselhaus, and Q. Xiong, "Interlayer breathing and shear modes in few-trilayer MoS<sub>2</sub> and WSe<sub>2</sub>," *Nano Lett.* **13**, 1007 (2013).
- [59] A. Molina-Sánchez and L. Wirtz, "Phonons in single-layer and few-layer MoS<sub>2</sub> and WS<sub>2</sub>," *Phys. Rev. B* **84**, 155413 (2011).
- [60] B. Chakraborty, H. S. S. R. Matte, A. K. Sood, and C. N. R. Rao, "Layer-dependent resonant Raman scattering of a few layer MoS<sub>2</sub>," *J. Raman Spectrosc.* **44**, 92 (2013).
- [61] W. Zhang, J.-K. Huang, C.-H. Chen, Y.-H. Chang, Y.-J. Cheng, and L.-J. Li, "High-gain phototransistors based on a CVD MoS<sub>2</sub> monolayer," *Adv. Mater.* **25**, 3456 (2013).
- [62] X. Zhang, W. Han, J. Wu, S. Milana, Y. Lu, Q. Li, A. Ferrari, and P. Tan, "Raman spectroscopy of shear and layer breathing modes in multilayer MoS<sub>2</sub>," *Phys. Rev. B* **87**, 115413 (2013).
- [63] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, and J. N. Coleman, "Liquid exfoliation of layered materials," *Science* **340**, 1226419 (2013).
- [64] F. Torrisi, T. Hasan, W. Wu, Z. Sun, A. Lombardo, T. S. Kulmala, G.-W. Hsieh, S. Jung, F. Bonaccorso, P. J. Paul, D. Chu, and A. C. Ferrari, "Inkjet-printed graphene electronics," *ACS Nano* **6**, 2992 (2012).
- [65] F. Withers, H. Yang, L. Britnell, A. P. Rooney, E. Lewis, A. Felten, C. R. Woods, V. Sanchez Romaguera, T. Georgiou, A. Eckmann, Y. J. Kim, S. G. Yeates, S. J. Haigh, A. K. Geim, K. S. Novoselov, and C. Casiraghi, "Heterostructures produced from nanosheet-based inks," *Nano Lett.* **14**, 3987 (2014).
- [66] H. Zhang, S. B. Lu, J. Zheng, J. Du, S. C. Wen, D. Y. Tang, and K. P. Loh, "Molybdenum disulfide (MoS<sub>2</sub>) as a broadband saturable absorber for ultra-fast photonics," *Opt. Express* **22**, 7249 (2014).
- [67] Z. Sun, T. Hasan, and A. C. Ferrari, "Ultrafast lasers mode-locked by nanotubes and graphene," *Physica E* **44**, 1082 (2012).
- [68] B. V. Cunning, C. L. Brown, and D. Kiepiński, "Low-loss flake-graphene saturable absorber mirror for laser mode-locking at sub-200-fs pulse duration," *Appl. Phys. Lett.* **99**, 261109 (2011).
- [69] B. Xu, Y. Cheng, Y. Wang, Y. Huang, J. Peng, Z. Luo, H. Xu, Z. Cai, J. Weng, and R. Moncorgé, "Passively Q-switched Nd:YAlO<sub>3</sub> nanosecond laser using MoS<sub>2</sub> as saturable absorber," *Opt. Express* **22**, 28934 (2014).
- [70] R. J. Smith, P. J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G. S. Duesberg, J. C. Grunlan, G. Moriarty, J. Chen, J. Wang, A. I. Minett, V. Nicolosi, and J. N. Coleman, "Large-scale exfoliation of inorganic layered compounds in aqueous surfactant solutions," *Adv. Mater.* **23**, 3944 (2011).
- [71] R. I. Woodward, E. J. R. Kelleher, T. H. Runcorn, S. V. Popov, F. Torrisi, R. C. T. Howe, and T. Hasan, "Q-switched fiber laser with MoS<sub>2</sub> saturable absorber," in *CLEO: 2014, OSA Technical Digest (Optical Society of America, 2014)*, paper SM3H-6.
- [72] R. I. Woodward, E. J. R. Kelleher, R. C. T. Howe, G. Hu, F. Torrisi, T. Hasan, S. V. Popov, and J. R. Taylor, "Tunable Q-switched fiber laser based on saturable edge-state absorption in few-layer molybdenum disulfide (MoS<sub>2</sub>)," *Opt. Express* **22**, 31113 (2014).
- [73] M. Zhang, R. C. T. Howe, R. I. Woodward, E. J. R. Kelleher, F. Torrisi, G. Hu, S. V. Popov, J. R. Taylor, and T. Hasan, "Solution processed MoS<sub>2</sub>-PVA composite for sub-bandgap mode-locking of a wide-band tunable ultrafast Er:fiber laser," *Nano Res.*, DOI 10.1007/s12274-014-0637-2 (posted 14 November 2014, in press).
- [74] Y. Huang, Z. Luo, Y. Li, M. Zhong, B. Xu, K. Che, H. Xu, Z. Cai, J. Peng, and J. Weng, "Widely-tunable, passively Q-switched erbium-doped fiber laser with few-layer MoS<sub>2</sub> saturable absorber," *Opt. Express* **22**, 25258 (2014).
- [75] Z. Luo, Y. Huang, M. Zhong, Y. Li, J. Wu, B. Xu, H. Xu, Z. Cai, J. Peng, and J. Weng, "1-, 1.5-, and

- 2-um fiber lasers Q-switched by a broadband few-layer MoS<sub>2</sub> saturable absorber,” *J. Lightwave Technol.* **32**, 4077 (2014).
- [76] R. Khazaeinezhad, S. H. Kassani, T. Nazari, H. Jeong, J. Kim, K. Choi, J.-U. Lee, J. H. Kim, H. Cheong, D.-I. Yeom, and K. Oh, “Saturable optical absorption in MoS<sub>2</sub> nano-sheet optically deposited on the optical fiber facet,” *Opt. Commun.* **335**, 224 (2015).
- [77] H. Xia, H. Li, C. Lan, C. Li, X. Zhang, S. Zhang, and Y. Liu, “Ultrafast erbium-doped fiber laser mode-locked by a CVD-grown molybdenum disulfide (MoS<sub>2</sub>) saturable absorber,” *Opt. Express* **22**, 17341 (2014).
- [78] R. Khazaeizhad, S. H. Kassani, H. Jeong, D.-I. Yeom, and K. Oh, “Mode-locking of Er-doped fiber laser using a multilayer MoS<sub>2</sub> thin film as a saturable absorber in both anomalous and normal dispersion regimes,” *Opt. Express* **22**, 23732 (2014).
- [79] H. Li, H. Xia, C. Lan, C. Li, X. Zhang, J. Li, and Y. Liu, “Passively Q-switched Erbium-doped fiber laser based on few-layer MoS<sub>2</sub> saturable absorber,” *IEEE Photon. Technol. Lett.* **27**, 69 (2015).
- [80] A. R. Beal, J. C. Knights, and W. Y. Liang, “Transmission spectra of some transition metal dichalcogenides. II. Group VIA: trigonal prismatic coordination,” *J. Phys. C* **5**, 3540 (1972).
- [81] R. A. Bromley, R. B. Murray, and A. D. Yoffe, “The band structures of some transition metal dichalcogenides: III. Group VIA : trigonal prism materials,” *J. Phys. C* **5**, 759 (1972).
- [82] H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier, and D. Baillargeat, “From bulk to monolayer MoS<sub>2</sub>: evolution of Raman scattering,” *Adv. Funct. Mater.* **22**, 1385 (2012).
- [83] T. Hasan, F. Torrisi, Z. Sun, D. Popa, V. Nicolosi, G. Privitera, F. Bonaccorso, and A. C. Ferrari, “Solution-phase exfoliation of graphite for ultrafast photonics,” *Phys. Status Solidi B* **247**, 2953 (2010).
- [84] N. Kumar, S. Najmaei, Q. Cui, F. Ceballos, P. Ajayan, J. Lou, and H. Zhao, “Second harmonic microscopy of monolayer MoS<sub>2</sub>,” *Phys. Rev. B* **87**, 161403 (2013).
- [85] R. Wang, H.-C. Chien, J. Kumar, N. Kumar, H.-Y. Chiu, and H. Zhao, “Third-harmonic generation in ultrathin films of MoS<sub>2</sub>,” *ACS Appl. Mater. Interfaces* **6**, 314 (2014).
- [86] Y. Li, Y. Rao, K. F. Mak, Y. You, S. Wang, C. R. Dean, and T. F. Heinz, “Probing symmetry properties of few-layer MoS<sub>2</sub> and h-BN by optical second-harmonic generation,” *Nano Lett.* **13**, 3329 (2013).
- [87] R. Sundaram, M. Engel, A. Lombardo, R. Krupke, A. C. Ferrari, P. Avouris, and M. Steiner, “Electroluminescence in single layer MoS<sub>2</sub>,” *Nano Lett.* **13**, 1416 (2013).
- [88] M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. Hagan, and E. Van Stryland, “Sensitive measurement of optical nonlinearities using a single beam,” *IEEE J. Quant. Electron.* **26**, 760 (1990).
- [89] B. Taheri, H. Liu, B. Jassemejjad, D. Appling, R. C. Powell, and J. J. Song, “Intensity scan and two photon absorption and nonlinear refraction of C60 in toluene,” *Appl. Phys. Lett.* **68**, 1317 (1996).
- [90] R. F. Souza, M. A. R. C. Alencar, J. M. Hickmann, R. Kobayashi, and L. R. P. Kassab, “Femtosecond nonlinear optical properties of tellurite glasses,” *Appl. Phys. Lett.* **89**, 171917 (2006).
- [91] E. Garmire, “Resonant optical nonlinearities in semiconductors,” *IEEE J. Sel. Top. Quantum Electron.* **6**, 1094 (2000).
- [92] T. R. Schibli, E. R. Thoen, F. X. Kärtner, and E. P. Ippen, “Suppression of Q-switched mode locking and break-up into multiple pulses by inverse saturable absorption,” *Appl. Phys. B* **49**, 41 (2000).
- [93] K. Wang, Y. Feng, C. Chang, J. Zhan, C. Wang, Q. Zhao, J. N. Coleman, L. Zhang, W. Blau, and J. Wang, “Broadband ultrafast nonlinear absorption and nonlinear refraction of layered molybdenum dichalcogenide semiconductors,” *Nanoscale* **6**, 10530 (2014).
- [94] R. Wang, B. A. Ruzicka, N. Kumar, M. Z. Bellus, H.-Y. Chiu, and H. Zhao, “Ultrafast and spatially resolved studies of charge carriers in atomically thin molybdenum disulfide,” *Phys. Rev. B* **86**, 045406 (2012).
- [95] Q. Ouyang, H. Yu, K. Zhang, and Y. Chen, “Saturable absorption and the changeover from saturable absorption to reverse saturable absorption of MoS<sub>2</sub> nanoflake array films,” *J. Mater. Chem. C* **2**, 6319 (2014).
- [96] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer, 2010).
- [97] S. Kasap, *Principles of Electronic Materials and Devices* (McGraw-Hill, 2005).
- [98] C. B. Roxlo, M. Daage, A. F. Ruppert, and R. R. Chianelli, “Optical absorption and catalytic activity of molybdenum sulfide edge surfaces,” *J. Catal.* **100**, 176 (1986).
- [99] C. B. Roxlo, M. Daage, D. P. Leta, K. S. Liang, S. Rice, A. F. Ruppert, and R. R. Chianelli, “Catalytic defects at molybdenum disulfide “edge” planes,” *Solid State Ionics* **22**, 97 (1986).
- [100] C. B. Roxlo, “Bulk and surface optical absorption in molybdenum disulfide,” *J. Vac. Sci. Technol. A* **5**, 555 (1987).
- [101] X. Yin, Z. Ye, D. A. Chenet, Y. Ye, K. O’Brien, J. C. Hone, and X. Zhang, “Edge nonlinear optics on a MoS<sub>2</sub> atomic monolayer,” *Science* **344**, 48 (2014).
- [102] M. I. Demchuk, N. V. Kuleshov, and V. P. Mikhailov, “Saturable absorbers based on impurity and defect centers in crystals,” *IEEE J. Quant. Electron.* **30**, 2120 (1994).
- [103] Z. Zhang, L. Qian, D. Fan, and X. Deng, “Gallium arsenide: A new material to accomplish passively mode-locked Nd:YAG laser,” *Appl. Phys. Lett.* **60**, 419 (1992).
- [104] M. E. Fermann and I. Hartl, “Ultrafast fibre lasers,” *Nature Photonics* **7**, 868 (2013).
- [105] A. K. M. Newaz, D. Prasai, J. I. Ziegler, D. Caudel, S. Robinson, R. F. Haglund Jr, and K. I. Bolotin, “Electrical control of optical properties of monolayer MoS<sub>2</sub>,” *Solid State Comm.* **155**, 49 (2013).
- [106] Z. Yin, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen, and H. Zhang, “Single-layer MoS<sub>2</sub> phototransistors,” *ACS Nano* **6**, 74 (2012).
- [107] D.-S. Tsai, K.-K. Liu, D.-H. Lien, M.-L. Tsai, C.-F. Kang, C.-A. Lin, L.-J. Li, and J.-H. He, “Few-layer MoS<sub>2</sub> with high broadband photogain and fast optical switching for use in harsh environments,” *ACS Nano* **7**, 3905 (2013).
- [108] M. Bernardi, M. Palummo, and J. C. Grossman, “Extraordinary sunlight absorption and one nanometer

- thick photovoltaics Using two-dimensional monolayer materials,” *Nano Lett.* **13**, 3664 (2013).
- [109] M.-L. Tsai, S.-H. Su, J.-K. Chang, D.-S. Tsai, C.-H. Chen, C.-I. Wu, L.-J. Li, L.-J. Chen, and J.-H. He, “Monolayer MoS<sub>2</sub> Heterojunction Solar Cells,” *ACS Nano* **8**, 8317 (2014).
  - [110] L. M. Malard, T. V. Alencar, A. P. M. Barboza, K. F. Mak, and A. M. de Paula, “Observation of intense second harmonic generation from MoS<sub>2</sub> atomic crystals,” *Phys. Rev. B* **87**, 201401 (2013).
  - [111] K. F. Mak, K. He, J. Shan, and T. F. Heinz, “Control of valley polarization in monolayer MoS<sub>2</sub> by optical helicity,” *Nat. Nanotechnol.* **7**, 494 (2012).
  - [112] H. Zeng, J. Dai, W. Yao, D. Xiao, and X. Cui, “Valley polarization in MoS<sub>2</sub> monolayers by optical pumping,” *Nat. Nanotechnol.* **7**, 490 (2012).
  - [113] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, B. Liu, and J. Feng, “Valley-selective circular dichroism of monolayer molybdenum disulphide,” *Nat. Commun.* **3**, 887 (2012).
  - [114] H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund, S. T. Pantelides, and K. I. Bolotin, “Bandgap engineering of strained monolayer and bilayer MoS<sub>2</sub>,” *Nano Lett.* **13**, 3626 (2013).
  - [115] K. Roy, M. Padmanabhan, S. Goswami, T. P. Sai, G. Ramalingam, S. Raghavan, and A. Ghosh, “Graphene-MoS<sub>2</sub> hybrid structures for multifunctional photoresponsive memory devices,” *Nat. Nanotechnol.* **8**, 826 (2013).
  - [116] W. Zhang, C.-P. Chuu, J.-K. Huang, C.-H. Chen, M.-L. Tsai, Y.-H. Chang, C.-T. Liang, Y.-Z. Chen, Y.-L. Chueh, J.-H. He, M.-Y. Chou, and L.-J. Li, “Ultrahigh-gain photodetectors based on atomically thin graphene-MoS<sub>2</sub> heterostructures,” *Sci. Rep.* **4**, 3826 (2014).
  - [117] G. Eda and S. A. Maier, “Two-dimensional crystals: managing light for optoelectronics,” *ACS Nano* **7**, 5660 (2013).
  - [118] N. Huo, J. Kang, Z. Wei, S.-S. Li, J. Li, and S.-H. Wei, “Novel and Enhanced Optoelectronic performances of multilayer MoS<sub>2</sub>WS<sub>2</sub> heterostructure transistors,” *Adv. Funct. Mater.* **24**, 7025 (2014).
  - [119] H. Wang, F. Liu, W. Fu, Z. Fang, W. Zhou, and Z. Liu, “Two-dimensional heterostructures: fabrication, characterization, and application,” *Nanoscale* **6**, 12250 (2014).
  - [120] Y. Y. Wang, F. Couny, P. S. Light, B. J. Mangan, and F. Benabid, “Compact and portable multiline UV and visible Raman lasers in hydrogen-filled HC-PCF,” *Opt. Lett.* **35**, 1127 (2010).
  - [121] D. J. Richardson, J. Nilsson, and W. A. Clarkson, “High power fiber lasers: current status and future perspectives,” *J. Opt. Soc. Am. B* **27**, B63 (2010).
  - [122] B. Ortaç, M. Baumgartl, J. Limpert, and A. Tünnermann, “Approaching microjoule-level pulse energy with mode-locked femtosecond fiber lasers,” *Opt. Lett.* **34**, 1585 (2009).
  - [123] W. Renninger, A. Chong, and F. Wise, “Giant-chirp oscillators for short-pulse fiber amplifiers,” *Opt. Lett.* **33**, 3025 (2008).
  - [124] R. I. Woodward, E. J. R. Kelleher, T. H. Runcorn, S. Loranger, D. Popa, V. J. Wittwer, A. C. Ferrari, S. V. Popov, R. Kashyap, and J. R. Taylor, “Fiber grating compression of giant-chirped nanosecond pulses from an ultra-long nanotube mode-locked fiber laser,” *Opt. Lett.* **40**, 387 (2015).
  - [125] A. Giesen and J. Speiser, “Fifteen years of work on thin-disk lasers: results and scaling laws,” *IEEE J. Sel. Top. Quantum Electron.* **13**, 598 (2007).
  - [126] K. Wu, X. Zhang, J. Wang, X. Li, and J. Chen, “WS<sub>2</sub> as a saturable absorber for ultrafast photonic applications of mode-locked and Q-switched lasers,” arXiv:1411.5777 (posted 21 November 2014).
  - [127] S. H. Kassani, R. Khazaeizhad, H. Jeong, D.-I. Yeom, and K. Oh, “All-fiber Er-doped Q-switched laser based on Tungsten Disulfide saturable absorber,” *Opt. Mater. Express* **5**, 373 (2015).
  - [128] D. Mao, Y. Wang, C. Ma, L. Han, B. Jiang, X. Gan, S. Hua, W. Zhang, T. Mei, and J. Zhao, “WS<sub>2</sub> mode-locked ultrafast fiber laser,” *Sci. Rep.* **5**, 7965 (2015).
  - [129] P. Yan, A. Liu, Y. Chen, H. Chen, S. Ruan, S. Chen, I. L. Li, H. Yang, J. Hu, and G. Cao, “Microfiber-based WS<sub>2</sub>-film saturable absorber for ultra-fast photonics,” *Optics Materials Express* **5**, 479 (2015).